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OBSERVATIONS
ON THE
CONSTITUENTS OF ALOES

BY

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The primary object of the present investigation of aloes was to ascertain whether any anthraquinone derivative other than aloe-emodin is contained therein. Although the hope of isolating small amounts of such compounds as emodin and chrysophanol was not realised, the results which have been obtained would appear worthy of record.

The material employed consisted of a good quality of Curaçao aloes. One kilogram of this material was crushed, mixed with water, and distilled in a current of steam, when a small amount (about 1 gramme) of a very strong smelling essential oil was obtained. Such an essential oil, possessing the characteristic odour of the drug, had previously been obtained by T. and H. Smith, of Edinburgh (*Pharm. Journ.*, 1880 [iii.], 10, 613).

The dark-coloured solution of the aloes in the distillation flask was then evaporated to dryness on purified sawdust. This operation naturally caused the resinification of the aloin, but that was immaterial for the purpose of the present investigation. The thoroughly dried mixture was then successively extracted in a Soxhlet apparatus with petroleum (b.p. 35-50°), ether, chloroform, ethyl acetate, and alcohol, each of the extracts being separately examined.

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The petroleum extract, which was small in amount, was boiled with a large volume of water, and the mixture cooled and filtered. On extracting the filtrate with ether a small amount of a crystalline acid was obtained which gave a violet colouration with ferric chloride, and appeared to be salicylic acid, but the amount was much too small for analysis.

The portion of the petroleum extract which was insoluble in water consisted chiefly of aloe-emodin. It was dissolved in chloroform and fractionally extracted with aqueous alkalis of varying strengths, but the presence of no other anthraquinone derivative was revealed. The above-mentioned aloe-emodin melted at a temperature a little higher than that usually recorded, namely, at 225° .

0.1212 gave 0.2958 CO_2 and 0.0401 H_2O . $\text{C}=66.6$; $\text{H}=3.7$.

$\text{C}_{15}\text{H}_{10}\text{O}_5$ requires $\text{C}=66.7$; $\text{H}=3.7$ per cent.

On benzylation in pyridine solution it yielded tribenzoylaloë-emodin, melting at $233-234^{\circ}$.

The neutral portion of the petroleum extract, which remained dissolved in the chloroform after extraction with alkalis, was hydrolysed with alcoholic potassium hydroxide. It then yielded a small amount of fatty acid, which, when recrystallised from alcohol, melted at $75-78^{\circ}$.

The ether and chloroform extracts of the aloes were found to consist largely of aloe-emodin, together with some amorphous material. The aloe-emodin was carefully examined as before for the presence of other anthraquinone derivatives, but with a negative result.

The ethyl acetate extract of the aloes represented about 39 per cent. of the material. It was dissolved in alcohol, and as much as possible of the aloe-emodin removed by crystallisation. The filtrate was then poured into water and deprived of alcohol by means of a current of steam, when, on cooling, it deposited a quantity of resinous material. The aqueous liquid was then extracted many times with amyl alcohol, when a considerable quantity of amorphous, deliquescent material was removed. The aqueous liquid was finally treated with basic lead acetate, the mixture filtered, the excess of lead removed by means of hydrogen sulphide, and the liquid again filtered and concentrated. It then yielded *d*-phenylglucosazone (m.p. 211°), thus showing the presence of sugar in the aloes.

Several investigators have stated that aloes contains some glucosidic material, and Léger (*J. Pharm. Chim.*, 1904 [vi.], 20, 145) has shown that aloin, under certain conditions, can yield a pentose. It has also been shown that, when hydrolysed with acids and with alkalis, aloes yields either *p*-coumaric acid or cinnamic acid. Thus, Hlasiwetz (*Annalen*, 1865, 136, 31) and Eigel (*Ber.*, 1887, 20, 2527) obtained the former acid by this means, whilst Tschirch and Pedersen (*Arch. Pharm.*, 1898, 236, 200) and Tschirch and Hoffbauer (*ibid.*, 1905, 243, 399) have stated that Curaçao aloes yields only cinnamic acid and Zanzibar aloes only *p*-coumaric acid.

In view of these statements, both the resinous material mentioned above and the deliquescent product extracted by amyl alcohol were submitted to acid and to alkaline hydrolysis.

The acid hydrolyses, both of which yielded similar results, were conducted in the following manner:—The material was dissolved in hot, dilute alcohol, and such an amount of sulphuric acid added as would correspond to 10 per cent. of the liquid. The mixture was then boiled for some time, after which it was cooled and extracted with ether. The ethereal liquid was then shaken successively with aqueous ammonium carbonate and potassium hydroxide. The ammonium carbonate extract, on acidification, yielded a product which, on crystallisation from water, gave cinnamic acid, melting at 230-231°. The potassium hydroxide extract, when acidified, gave aloe-emodin. The acid, aqueous liquid which had been extracted with ether was then deprived of some amorphous material by extraction with amyl alcohol, after which the sulphuric acid was removed by treatment with barium hydroxide. The filtered liquid, after concentration, then yielded *d*-phenylglucosazone, which melted at 212°. A careful examination was made for the osazone of a pentose, but none was present. It is evident, therefore, that aloes contains a small amount of glucosidic material.

For the purpose of the alkaline hydrolyses the products were dissolved in dilute, aqueous potassium hydroxide, and the mixture boiled for a short time. The liquid was then acidified, and extracted with ether, after which the ethereal liquid was shaken with aqueous ammonium carbonate. On acidifying the ammonium carbonate extract, and extracting it with ether, a moderate amount of an acid product was obtained, which appeared to be a mixture. It was, therefore, esterified with absolute alcohol, and the resulting esters

isolated by means of ether. The ethereal liquid was first deprived of a small amount of unesterified acid by means of aqueous sodium carbonate, after which it was shaken with dilute, aqueous potassium hydroxide for the removal of any phenolic ester. The alkaline liquid so obtained, after being heated to hydrolyse the ester, yielded *p*-coumaric acid, which melted at 204-205°.

0.1226 gave 0.2968 CO₂ and 0.0525 H₂O. C = 65.7; H = 4.9.

C₉H₈O₃ requires C = 65.8; H = 4.9 per cent.

The ethereal liquid from which the ethyl *p*-coumarate had been removed by means of aqueous potassium hydroxide was evaporated, and the residue, which was somewhat brown in colour, distilled in a current of steam. A colourless, volatile ester then passed over, which, on hydrolysis, yielded cinnamic acid, melting at 231-232°.

0.1355 gave 0.3631 CO₂ and 0.0646 H₂O. C = 73.0; H = 5.4.

C₉H₈O₂ requires C = 73.0; H = 5.4 per cent.

The alcohol extract of the aloes was similar to that obtained by means of ethyl acetate, and yielded analogous results on hydrolysis. It is evident, therefore, that Curaçao aloes yields both cinnamic and *p*-coumaric acids, and not only the former, as was stated by Tschirch and Hoffbauer (*loc. cit.*).

Tschirch and Pedersen (*loc. cit.*) have stated that they succeeded in obtaining aloë-emodin by passing air through an alkaline solution of aloin. A number of commercial samples of aloin were, therefore, investigated in this direction by the present authors, but it was found that even when oxygen was passed for many hours through a warm solution of aloin in dilute aqueous potassium hydroxide no aloë-emodin was formed. Several commercial samples of aloin were, however, already found to contain aloë-emodin as an impurity, and it is possible that the observation of Tschirch and Pedersen may thus be explained.

